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An efficient synthesis of 14-substituted-14*H*-dibenzo[*a,j*]xanthene derivatives promoted by a nano isopolyoxomolybdate under thermal and solvent-free conditions

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Abstract: Synthesis of 14-substituted-14*H*-dibenzo[*a,j*]xanthene derivatives using the condensation of *β*-naphthol with wide range of various aldehydes in the presence of a Keplerate type giant nanoporous isopolyoxomolybdate, $(NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$, represented as $\{Mo_{132}\}$, as an efficient catalyst under solvent free condition is reported. The catalyst was prepared according to a previously published literature procedure using inexpensive and readily available starting materials. Furthermore, the catalyst could be recovered conveniently and reused efficiently such that a considerable catalytic activity still could be achieved after fifth run. Other beneficial features of this new synthetic approach include short reaction times, high yields, clean reaction profiles, and a simple work-up procedure.

Keywords: Giant nanoporous isopolyoxomolybdate, Keplerate, $\{Mo_{132}\}$, 14-substituted-14*H*-dibenzo[*a,j*]xanthene, Solvent-free.

Introduction

Polyoxometalates (POMs) are a large class of metal oxide clusters of early transition metals, typically W(VI), V(V), Mo(VI), Nb(V) and Ta (V), bridged by oxygen atoms. They are of proven value in catalysis, magnetism, materials science and biomedicine [1–5]. Because they are diverse and highly modifiable in size, shape, charge density, acidity and reversible redox potential. A number of very large POM anions have been synthesized and structurally characterized. Beginning with the big-wheel Mo_{154} anion [6], Müller's group have reported several giant mixed-valence POMs with cyclic (Mo_{176}) [7], capped cyclic (Mo_{248}) [8], and basket (Mo_{116}) [9] architectures.

Giant nanosized porous Keplerate-type POMs show a large variety of applications in fundamental and applied science, such as in modelling passive cation transport through membranes, encapsulation, nanoseparation chemistry and magnetic and optics applications [10, 11]. In spite of these valuable properties, despite various compounds have been used as catalysts in organic synthesis [12–24], application of giant nanosized porous POMs as catalysts in organic transformations has been largely overlooked [25]. Müller and co-workers, for the first time, reported the synthesis of a Keplerate-type giant-ball nanoporous isopolyoxomolybdate which was formulated as $(NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$ and denoted as $\{Mo_{132}\}$ [26] Recently, the application of $\{Mo_{132}\}$ as a catalyst has been reported for a series of organic transformations by our group. This new reusable catalyst performed well and showed a high level of catalytic activity in the synthesis of 1,2,4,5-tetrasubstituted imidazoles, 1,8-dioxo octahydr
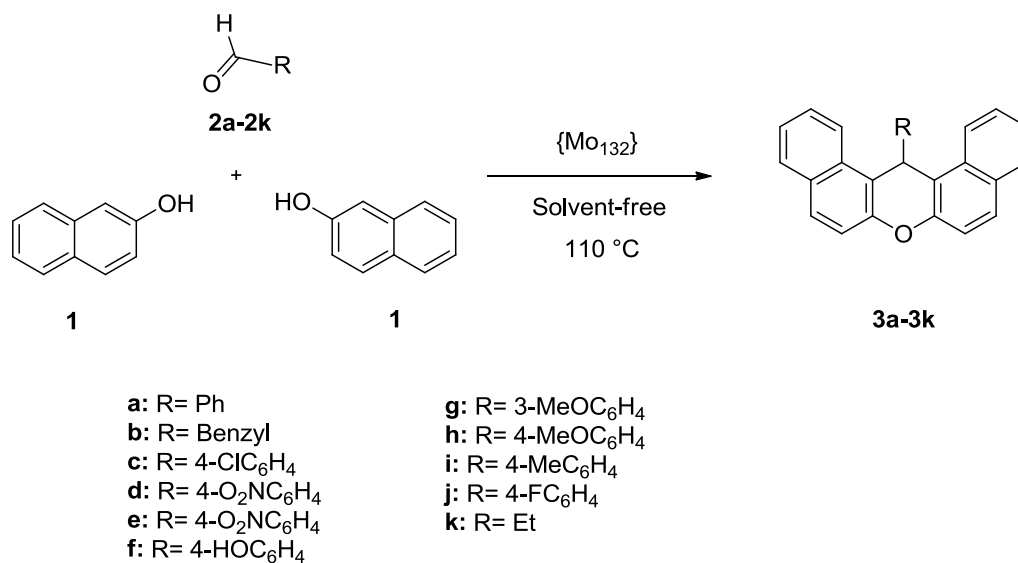
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oxanthenes, 1,8-dioxodecahydroacridines and poly hydroquinolines [55–57]. Benzoxanthenes are an important class of organic compounds with low molecular weight which have broad spectrum of biological and therapeutic properties such as antiviral [27], antibacterial [28], and anti-inflammatory [29], activities, anti-proliferative activity [30] and efficiency in photodynamic therapy [31], Furthermore, these compounds can be employed as dyes [32], pH-sensitive fluorescent materials for visualization of biomolecules [33], and in laser technologies [34]. For the construction of xanthenes and benzoxanthenes, various procedures are available including the cycloacylation of carbamates [35], trapping of benzynes by phenol [36], cyclocondensation between 2-hydroxy aromatic aldehydes and 2-tetralone [37], cyclodehydrations [38], and intramolecular phenyl carbonyl reaction of aldehydes with β-naphthol by dehydration [39]. Other ways for the synthesis of benzoxanthenes and related products include the reaction of β-naphthol with formamide [40], carbon monoxide [41], and 2-hydoxynaphth-1-ylmethanol [42]. Various reagents have been employed for the synthesis of benzoxanthenes such as $CoPy_2Cl_2$ [43], $Al(HSO_4)_3$ [44], H_3NSO_3 [45], Selectfluor™ [46], I_2 [47], Amberlyst-15 [48], $K_5CoW_{12}O_{40} \cdot 3H_2O$ [49], $K_{12}[As_2W_{18}Cu_3O_{68}] \cdot 30H_2O$ [50], [Hmim][HSO_4] [51], H_2SO_4 in acetic acid as solvent [52], $NH_4H_2PO_4/SiO_2$ [53], and $Sc[N(SO_2C_8F_{17})_2]_3$ [54], as catalysts. Major drawbacks of these procedures include expensive reagents, use of large amounts of toxic organic solvents, prolonged heating and side reactions. All of these disadvantages make further improvement of the synthesis of such molecules essential. Therefore, the development of a new greener and more convenient method using a new catalyst with high catalytic activity for the synthesis of 14-substituted-14*H*-dibenzo[*a,j*]xanthene is highly desirable. As part of our research program on the development of convenient methods using reusable catalysts for the synthesis of organic compounds [55–62]. We report here the results of our investigation on the application of {Mo_{132}} as heterogeneous catalysts in the synthesis of 14-substituted-14*H*-dibenzo[*a,j*]xanthenes (Scheme **1**). The diameter of this ball-shaped POM which calculated theoretically is 2.9 nm [62–64]. For the first time this molybdenum cluster has been characterized by the TEM image by Polarz et al [9, 65]. The TEM picture clearly shows a periodic structure with an average size approximately 3 nm diameter. This experimentally obtained diameter fits nicely with the theoretical value for the inner diameter of the ball-shaped POM [62–64].

Results and discussion

The catalyst {Mo_{132}} was characterized by XRD, FT-IR and UV/Vis spectroscopy as reported in our previous work [55]. The catalytic activity of {Mo_{132}} was evaluated in the synthesis of 14-substituted-14*H*-dibenzo[*a,j*]xanthenes. At first, the synthesis of compound **3c** was selected as a model reaction to determine suitable reaction conditions. The reaction was carried out by mixture of 4-chlorobenzaldehydes (1 mmol), and β-naphthol (2 mmol) in the presence of {Mo_{132}} in different solvents such as H_2O, EtOH, MeOH, CH_2Cl_2, CH_3CN, and also solvent-free conditions at different temperature (Table **1**). It was found that the yield of compound **3c** was strongly affected by the catalyst amount and reaction temperature in solvent-free conditions. Low to moderate yields of the product was obtained in the absence of the catalyst at 110 °C (entry 1) or in the presence of the catalyst at room temperature (entry 2) indicating that the catalyst and temperature are necessary for the reaction. Increasing the amount of the catalyst and reaction temperature up to 0.08 g and 110 °C, respectively, increased the yield of the product **3c**, whereas further increase in both catalyst amount and temperature did not improve the product yield and reaction time (entry 15). Encouraged by this success, and in order to evaluate the generality of this model reaction, we extended the reaction of β-naphthol with a range of other aromatic/aliphatic aldehydes under the optimized reaction conditions. The {Mo_{132}} efficiently catalyzed the reactions, giving the products **3a-3k** in high yields over relatively short reaction times. Easy separation of obtained products from the catalyst makes this method useful for the synthesis of 14-substituted-14*H*-dibenzo[*a,j*]xanthenes. Purity checks with melting points, TLC, ^{13}C NMR, and ^{1}H NMR, spectroscopic data reveal that only one product is formed in all cases and no undesirable side-products are observed. The structures of all known products **3a-3k** were deduced from their ^{1}H NMR, ^{13}C NMR, FT-IR spectral data, and a comparison of their melting points with those of authentic samples.

a: R= Ph
b: R= Benzyl
c: R= 4-ClC$_6$H$_4$
d: R= 4-O$_2$NC$_6$H$_4$
e: R= 4-O$_2$NC$_6$H$_4$
f: R= 4-HOC$_6$H$_4$

g: R= 3-MeOC$_6$H$_4$
h: R= 4-MeOC$_6$H$_4$
i: R= 4-MeC$_6$H$_4$
j: R= 4-FC$_6$H$_4$
k: R= Et

Scheme 1. {Mo$_{132}$} catalyzed synthesis of 14-substituted-14*H*-dibenzo[*a,j*]xanthenes.

Table 1. Optimization of reaction conditions for synthesis of compound **3c** catalyzed by {Mo$_{132}$}[*].

Entry	Catalyst (g)	Solvent	T (°C)	Time (min)	Isolated yield (%)
1	-----	-----	110	65	-----
2	0.08	-----	r.t.	60	54
3	0.02	-----	90	40	58
4	0.02	-----	110	37	67
5	0.04	-----	90	35	78
6	0.04	-----	110	30	84
7	0.04	-----	120	30	81
8	0.06	-----	90	25	91
9	0.06	-----	110	20	94
10	0.06	-----	120	20	89
11	0.08	-----	90	15	94
12	0.08	-----	110	10	96
13	0.08	-----	120	12	93
14	0.10	-----	90	15	92
15	0.10	-----	110	10	91
16	0.08	CH$_2$Cl$_2$	Reflux	90	45
17	0.08	H$_2$O	Reflux	90	56
18	0.08	CH$_3$OH	Reflux	90	55
19	0.08	CH$_3$CH$_2$OH	Reflux	90	71
20	0.08	CH$_3$CN	Reflux	90	37

[*]Reaction condition: *β*-naphthol (2 mmol), and 4-chlorobenzaldehydes (1 mmol).

For example, the ^{1}H NMR, and ^{13}C NMR spectrum of **3i** in CDCl$_3$ are shown in Figure **1**, and Figure **2**; respectively. The ^{1}H NMR spectrum show a sharp singlet at δ 2.15 ppm related to a methyl group, and a singlet at δ 6.30 ppm for methine group as well as the signals at δ 6.45–8.80 ppm due to 16 aromatic protons indicating the formation of the compound **3i**. Also, the ^{13}C NMR signals in δ 20.89 ppm, and δ 37.62 ppm related to the methyl and methine groups, respectively,

and the signals in the aromatic region confirm the structure of compound **3i**. We compared the results we obtained using {Mo$_{132}$} as catalyst with previously reported results for the synthesis of 14-substituted-14H-dibenzo[*a,j*]xanthenes in the presence of various catalysts (Table **2**). Our reaction conditions showed shorter reaction times than all the other conditions and gave high yields of the desired products.
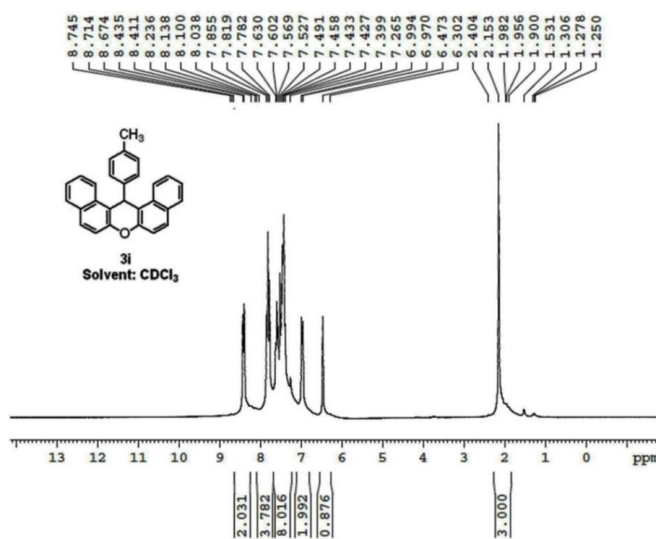

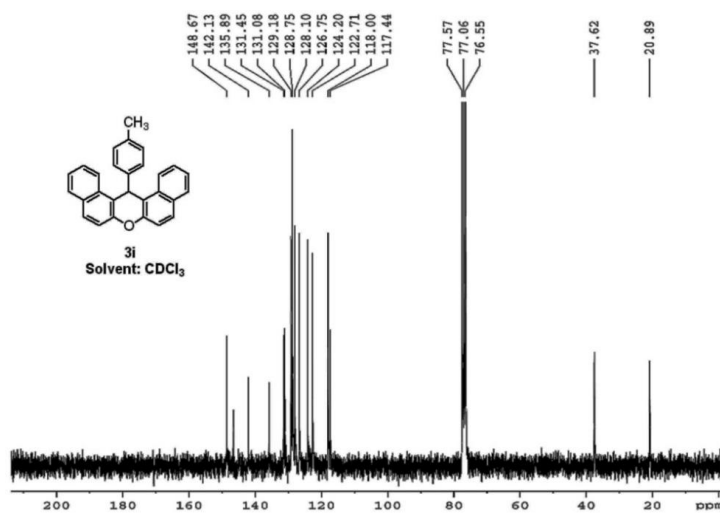**Figure 1.** The ^{1}H NMR spectrum of compound **3i** in CDCl$_3$ solvent.

Figure 2. The ^{13}C NMR spectrum of compound **3i** in CDCl$_3$ solvent.

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Table 2: Comparison of the efficiencies of different catalysts for the one-pot four-component synthesis of 14-substituted-14*H*-dibenzo[*a,j*]xanthenes.

Catalyst	Conditions			Time (min)	Yield (%)	Ref.
	Solvent	T/°C	Other			
CoPy$_2$Cl$_2$	-----	85	-----	90-480	65-97	[33]
Al(HSO$_4$)$_3$	-----	125	-----	20-43	85-91	[34]
H$_3$NSO$_3$	-----	125	-----	360-720	92-96	[35]
Selectfluor^{TM}	-----	125	-----	360-720	92-95	[36]
I$_2$	-----	90	-----	120-300	82-95	[37]
Amberlyst-15	-----	125	-----	20-120	82-94	[38]
K$_5$CoW$_{12}$O$_{40}$•3H$_2$O	-----	125	-----	60-120	74-97	[39]
K$_{12}$[As$_2$W$_{18}$Cu$_3$O$_{68}$]•30H$_2$O	-----	125	-----	150-240	76-95	[40]
[Hmim][HSO$_4$]	-----	125	-----	30-240	66-92	[41]
H$_2$SO$_4$	Acetic acid	75	-----	4320	60-90	[42]
NH$_4$H$_2$PO$_4$/SiO$_2$	Water	40	ultrasonic	40	85-94	[43]
Sc[N(SO$_2$C$_8$F$_{17}$)$_2$]$_3$	-----	110	-----	120-420	70-96	[44]
{Mo$_{132}$}	-----	110	-----	13-18	88-96	This work

We also used the model reaction under optimized reaction conditions to evaluate the reusability of the catalyst {Mo$_{132}$}. After completion of the reaction, the catalyst was recovered as described in the experimental section. The separated catalyst was washed with hot ethanol and subsequently dried at 50 °C under vacuum for 1 h before being reused in a similar reaction. We found that the catalyst could be used at least 5 times with only a slight reduction in activity (Figure **3**).
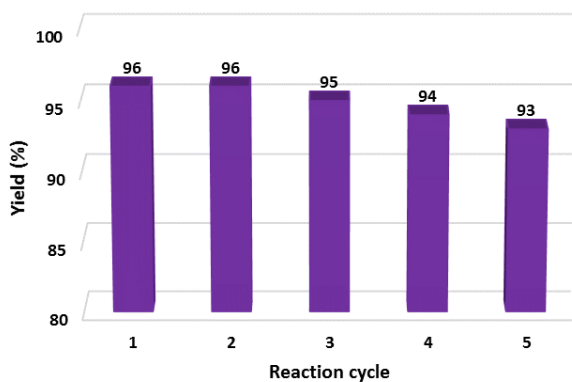
Figure 3. Effect of recycling on catalytic performance of {Mo$_{132}$} in the synthesis of **3c** in model reaction.

Although we did not investigate the reaction mechanism, a plausible mechanism for this reaction may proceed as depicted in Scheme **2**. It is reasonable to assume that several accessible Mo sites and NH$_4$ groups in {Mo$_{132}$} could act as Lewis acid and Brönsted acid centers respectively and therefore promote the necessary reactions. The catalyst would play a significant role in increasing the electrophilic character of the electrophiles in the reaction. According to this mechanism, the {Mo$_{132}$} catalyst would facilitate the formation of intermediates **I**, **II,** and **III**. Under these conditions, however, attempts to isolate the proposed intermediates failed even after careful monitoring of the reactions.

Experimental Section

All chemicals were available commercially and used without additional purification. The catalyst was synthesized according to the literature [26] Melting points were recorded using a Stuart SMP3 melting point apparatus. The FT-IR spectra of the products were obtained with KBr disks, using a Tensor 27 Bruker spectrophotometer. The ^{1}H NMR (300 MHZ), and ^{13}C NMR (75 MHZ) spectra were recorded using Bruker spectrometers.

General experimental procedure for the synthesis of 14-substituted-14H-dibenzo[a,j]xanthenes 3a-3k catalyzed by {Mo₁₃₂}:

A mixture of *β*- naphthol **1** (2 mmol), aromatic/aliphatic aldehyde **2** (1 mmol), and {Mo₁₃₂} (0.08 g) as catalyst was heated in the oil bath at 110 °C for 13-18 min. The reaction was monitored by TLC. Upon completion of the transformation, hot ethanol was added and the catalyst removed by filtration under hot conditions. The catalyst was washed with a small portion of hot ethanol. After cooling, the combined filtrate was allowed to stand at room temperature. The precipitated solid was collected by filtration, and recrystallized from ethanol to give compounds **3a-3k** in high yields.
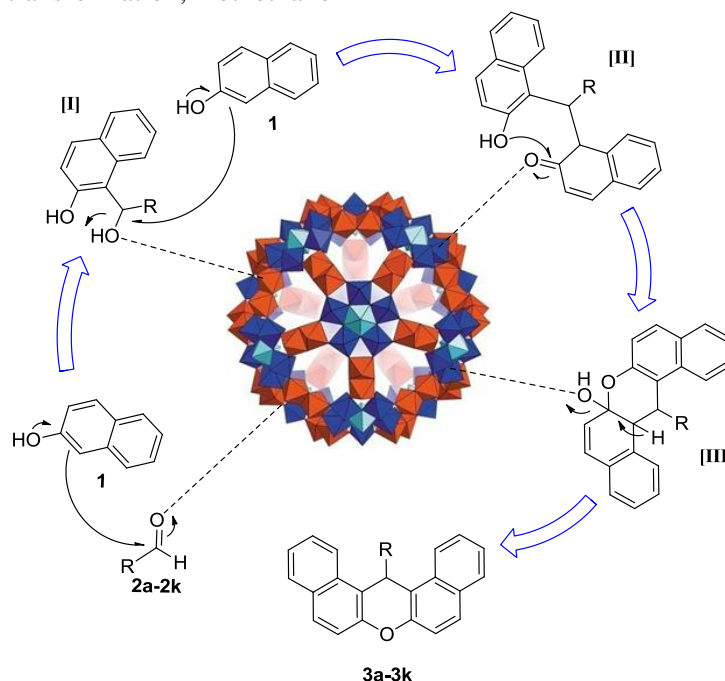
Scheme 2. Plausible mechanism for the {Mo₁₃₂}-catalyzed formation of 14-substituted-14*H*-dibenzo[*a,j*]xanthenes.

14-Phenyl-14H-dibenzo[a,j]xanthene (3a):

Yield: 94%; 15 min; M.p.: 182-184 °C (lit. [46] 183 °C); ^{1}H NMR (CDCl₃ , 300 MHz): δ 6.48 (s 1H, CH), 6.59 (t, *J* = 7.0 Hz, 1H, arom-H), 7.16 (t, *J* = 7.0 Hz, 2H, arom-H), 7.42 (t, *J* = 7.5 Hz, 2H, arom-H), 7.50-7.60 (m, 6H, arom-H), 7.76-7.85 (m, 4H, arom-H), 8.36 (d, *J* = 7.2 Hz, 2H,arom-H); ^{13}C NMR (CDCl₃ , 75 MHz): δ 37.8, 117.1, 118.4, 122.5, 124.6, 126.0, 126.5, 127.1, 128.3, 128.6, 129.1, 131.7, 131.9, 144.8, 148.6; IR (KBr, cm^{-1}): ν 3089, 3014, 2903, 1619, 1576, 1503, 1490, 1423, 1398, 1235, 1083, 1011, 947, 822, 734, 698.

14-benzyl-14-H-dibenzo[a,j]xanthene (3b):

Yield: 95%; 14 min; M.p.: 178-180 °C (lit. [53] 179 °C); ^{1}H NMR (CDCl₃ , 300 MHz): δ 3.31 (d, *J* = 5.1 Hz, 2H, CH₂), 5.76 (t, *J* = 5.1 Hz, 1H, CH), 6.21 (d, *J* = 8.6 Hz, 2H, arom-H), 6.80– 7.18 (m, 5H, arom-H), 7.43–7.87 (m, 8H, arom-H), 8.22 (d, *J* = 8.6 Hz, 2H, arom-H); ^{13}C NMR (CDCl₃ , 75 MHz): δ 33.4, 41.4,

115.2, 117.3, 122.2, 124.1, 126.1, 126.6, 127.2, 128.4, 128.8, 129.7, 130.8, 131.2, 137.6, 149.9; IR (KBr, cm^{-1}): ν 3060, 3017, 2921, 1617, 1585, 1510, 1490, 1432, 1379, 1233, 1078, 1003, 956, 841, 732, 686.

14-(4-Chlorophenyl)-14H-dibenzo[a,j]xanthene (3c):

Yield: 96%; 15 min; M.p.: 285-287 °C (lit. [46] 287 °C); ^{1}H NMR (CDCl₃ , 300 MHz): δ 6.69 (s, 1H, CH), 7.21 (d, *J* = 7.0 Hz, 2H, arom-H), 7.45–7.65 (m, 10H, arom-H), 7.95 (d, *J* = 7.79 Hz, 2H, arom-H), 8.69 (d, *J* = 7.6 Hz, 2H, arom-H); ^{13}C NMR (75 MHz, CDCl₃): δ 35.3, 117.7, 118.6, 123.5, 125.4, 127.8, 129.1, 129.6, 130.0, 130.4, 131.3, 131.5, 131.9, 145.6, 148.9; IR (KBr, cm^{-1}): 3133, 1618, 1590, 1450, 1225, 1105, 820, 776; IR (KBr, cm^{-1}): ν 3048, 2932, 1622, 1591,1449, 1436, 1395, 1252, 1039, 954, 831, 769, 658 cm^{-1}.

14-(4-Nitrophenyl)-14H-dibenzo[a,j]xanthene (3d):

Yield: 93%; 13 min; M.p.: 311-313 °C (lit. [46] 312 °C); ^{1}H NMR (CDCl₃ , 300 MHz): δ 6.57 (s, 1H, CH), 7.44 (t, *J* = 7.5 Hz, 2H, arom-H), 7.49 (d, *J* = 8.1 Hz,

2H, arom-H), 7.63 (t, *J* = 6.2 Hz, 2H, arom-H), 7.66 (d, *J* = 8.1 Hz, 2H, arom-H), 7.79 (d, *J* = 6.4 Hz, 2H, arom-H), 7.85 (d, *J* = 5.6 Hz, 2H, arom-H), 8.04 (d, *J* = 8.5 Hz, 2H, arom-H), 8.29 (d, *J* = 8.4 Hz, 2H, arom-H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 36.4, 116.2, 117.7, 123.1, 123.6, 124.7, 127.2, 128.7, 129.6, 130.7, 130.8, 135.1, 145.9, 148.1, 152.6; IR (KBr, cm^{-1}): ν 3078, 2946, 1626, 1609, 1594, 1449, 1403, 1341, 1207, 1138, 1100, 957, 827, 690.

14-(3-Nitrophenyl)-14H-dibenzo[a,i]xanthene-8,13-dione (3e):

Yield: 92%; 14 min; M.p.: 214-216 °C (lit. [46] 213 °C); ^{1}H NMR (CDCl$_3$, 300 MHz): δ 6.11 (s, 1H, CH), 7.50-7.40 (m, 3H, arom-H), 7.65-7.60 (m, 2H, arom-H), 7.80-7.78 (m, 6H, arom-H), 8.09 (s, 1H, arom-H), 8.15 (d, *J* = 7.0 Hz, 1H, arom-H), 8.19 (d, *J* = 7.0 Hz, 1H, arom-H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 35.2; 115.2, 115.3, 117.0, 122.1, 123.3, 124.9, 125.9, 127.8, 128.9, 129.4, 129.6, 130.1, 130.4, 130.6, 131.7, 132.0, 135.1, 135.3, 145.1, 147.3, 148.6, 157.7, 178.0, 178.1; IR (KBr, cm^{-1}): ν 3079, 2924, 1622, 1609, 1590, 1400, 1392, 1297, 1257, 1118, 1082, 1027, 953, 838, 801, 778.

14-(4-Hydroxyphenyl)-14H-dibenzo[a,j]xanthene (3f):

Yield: 89%; 16 min; M.p.: 139-140 °C (lit. [46] 140 °C); ^{1}H NMR (CDCl$_3$, 300 MHz): δ 4.96 (s br., 1H, OH), 6.34 (s, 1H, CH), 6.48 (d, *J* = 7.0 Hz, 2H, arom-H), 6.50-7.60 (m, 10H, arom-H), 7.63 (d, *J* = 7.0 Hz, 2H, arom-H), 8.28 (d, *J* = 7.2 Hz, 2H, arom-H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 37.8, 115.4, 117.9, 118.6, 122.9, 124.3, 127.4, 128.8, 129.3, 129.9, 131.4, 131.9, 137.9, 149.2, 154.2; IR (KBr, cm^{-1}): ν 3078, 2946, 1626, 1609, 1594, 1449, 1403, 1341, 1207, 1138, 1100, 957, 827, 690.

14-(3-Methoxyphenyl)-14H-dibenzo[a,j]xanthene (3g):

Yield: 93%; 15 min; M.p.: 163–164 °C (lit. [45] 164 °C); m.p.: °C. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 3.63 (s, 3H, OCH$_3$), 6.52 (s, 1H, CH), 7.00–6.55 (m, 4H, arom-H), 7.65–7.30 (m, 6H, arom-H), 7.80–7.75 (m, 4H, arom-H), 8.36 (d, *J* = 7.3 Hz 2H, arom-H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 38.6, 55.4, 111.8, 115.5, 116.8, 118.7, 121.0, 122.6, 124.4, 127.1, 128.4, 128.9, 129.3, 130.7, 131.4, 146.6, 149.1, 152.5; IR (KBr, cm^{-1}): ν 3068, 2952, 1621, 1612, 1589, 1447, 1411, 1352, 1212, 1123, 1089, 962, 831, 692.

14-(4-Methoxyphenyl)-14H-dibenzo[a,j]xanthene (3h):

Yield: 95%; 14 min; M.p.: 203–205 °C (lit. [46] 205 °C); ^{1}H NMR (CDCl$_3$, 300 MHz): δ 3.68 (s, 3H, CH$_3$), 6.51 (s, 1H, CH), 7.55–6.70 (m, 10H, arom-H), 7.75 (d, *J* = 7.2 Hz, 2H, arom-H), 7.85 (d, *J* = 7.2 Hz, 2H, arom-H), 8.39 (d, *J* = 7.3 Hz, 2H, arom-H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 37.6, 53.9, 114.3, 117.4, 118.8, 123.2, 125.3, 127.6, 128.8, 129.5, 131.6, 134.4, 137.1, 139.9, 150.4, 158.3; IR (KBr, cm^{-1}): ν 3069, 2924, 1613, 1589, 1502, 1466, 1423, 1400, 1252, 1112, 1079, 955, 833, 801, 751.

14-(4-Methylphenyl)-14H-dibenzo[a,j]xanthene (3i):

Yield: 94%; 14 min; M.p.: 227-229 °C (lit. [46] 228 °C); ^{1}H NMR (CDCl$_3$, 300 MHz): δ 2.15 (s, 3H, CH$_3$), 6.30 (s, 1H, CH), 6.97 (d, *J* = 7.2 Hz, 2H, arom-H), 7.35–7.65 (m, 8H, arom-H), 7.80-7.88 (m, 4H, arom-H), 8.41 (d, *J* = 7.2 Hz, 2H, arom-H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 20.9, 37.6, 117.4, 118.0, 122.7, 124.2, 126.7, 128.1, 128.7, 129.2, 131.1, 131.4 135.9, 142.1, 146.0, 148.7; IR (KBr, cm^{-1}): ν 3069, 2921, 1617, 1591, 1508, 1459, 1421, 1401, 1243, 1116, 1048, 979, 838, 744.

14-(3-Fluorophenyl)-14H-dibenzo[a,j]xanthene (3j):

Yield: 95%; 14 min; M.p.: 258-260 °C (lit. [46] 259 °C); ^{1}H NMR (CDCl$_3$, 300 MHz): δ 6.48 (s, 1H, CH) 6.70-8.35 (m, 16H, arom-H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 37.8, 89.9, 113.8, and 114.2 (*J* = 21.5 Hz, C–F), 115.6 and 115.9 (*J* = 21.5 Hz, C–F), 117.1, 118.2, 122.9, 124.31, and 124.34 (*J* = 2.8 Hz, C–F), 124.6, 127.8, 129.1, 129.4, 130.3, and 130.4 (*J* = 8.3 Hz, C–F), 131.7, and 131.9 (*J* = 19.4 Hz, C–F), 148.1, and 148.2 (*J* = 6.2 Hz, C–F), 149.5, 162.2, 165.5; IR (KBr, cm^{-1}): ν 3085, 2991, 1629, 1612, 1592, 1407, 1395, 1295, 1252, 1110, 1079, 1049, 945, 852, 808, 740.

14-Ethyl-14H-dibenzo[a,j]xanthene (3k):

Yield: 88%; 18 min; M.p.: 156-158 °C (lit. [54] 156-158 °C); mp 148–151 °C (lit. value 152 °C) (19). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 0.57 (t, *J* = 7.2 Hz, 3H, CH$_3$), 2.10-2.18 (m, 2H, CH$_2$), 5.62 (t, *J* = 4.3 Hz, 1H, CH), 7.36 (d, *J* = 7.5 Hz, 2H, arom-H), 7.45 (t, *J* = 7.2 Hz, 2H, arom-H), 7.60-7.90 (m, 6H, arom-H), 8.25 (d, *J* = 7.5 Hz, 2H, arom-H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 8.9, 28.6, 31.4, 115.6, 117.4, 122.5, 124.7, 126.8, 128.4, 129.3, 131.3, 131.8, 150.7; IR (KBr, cm^{-1}): ν 3062, 2926, 1623, 1588, 1049, 1395, 1252, 1110, 1080, 954, 848, 803, 742.

Conclusion

In conclusion, in this paper we showed that {Mo$_{132}$}, a Keplerate-type giant-ball nanoporous isopolyoxomolybdate, as a highly effective heterogeneous catalyst effectively catalyzes the reaction of *β*-naphthol with a range of aromatic or aliphatic aldehydes in solvent-free condition. This method provided 14-substituted-14*H*-dibenzo[*a,j*]xanthene products in high yields over short reaction time, following a facile work-up process. The catalyst is inexpensive and easily obtained, stable and storable, easily recycled and reused for several cycles with consistent activity.

Acknowledgments

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